SYNTHESIS AND CHARACTERISATION OF AMINE FUNCTIONALISED MAGNETIC SILICA NANOPARTICLE

A Dissertation

Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

By

Anjana Pattnaik

Under the Supervision of
Dr. Sasmita Mohapatra
DEPARTMENT OF CHEMISTRY

NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008, ORISSA

CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and characterization of Amine functionalized magnetite silica nanoparticle"** being submitted by Miss Anjana Pattnaik to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of partial fulfillment of the degree of Master of Science is a record of the research training carried out by her under my supervision and guidance. This work is a scale-up synthesis process of amine functionalized silica coated magnetite following the procedure earlier reported. The matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Rourkela
Date: 05-05-2011

Dr. Sasmita Mohapatra
Dept. of Chemistry
National Institute of Technology
Rourkela, Orissa

ACKNOWLEDGEMENT

With deep regards and profound respect, I avail the opportunity to express my deep sense of Gratitude and indebtedness to **Dr. Sasmita Mohapatra,** Department of Chemistry, National Institute of Technology, Rourkela for introducing the present project topic and for her inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I most gratefully acknowledge her constant encouragement and help in different ways to complete this project successfully.

I acknowledge my sincere regards to **Dr. B.G. Mishra (HOD)** and all the faculty members, Department of Chemistry, NIT Rourkela for their enthusiasm in promoting the research inchemistry and for their kindness and dedication to students. I specially record my deep appreciation and thanks to **Dr. B. G. Mishra**, **Dr. N. Panda**, **Dr. S.Patel**, **Dr. S. Chatterjee**, **Dr. A. Mondal** and their Ph.D scholars for giving me the necessary permission to use their laboratory facilities whenever I needed.

I would like to add a special note of thanks to **Mr. Smruti**, and **Ms. Swagatika** Ph.D. Scholars, Dept. of Chemistry for her kind help and guidance whenever required.

I acknowledge the support of my classmates throughout this course. Last but not the least, I also take the privilege to express my deep sense of gratitude to my parents, for selflessly extending their ceaseless help and moral support at all times.

Thanking you

Ms. Anjana Pattnaik

Roll No.:-409cy2020

M.Sc. Chemistry

N.I.T. Rourkela

CONTENTS

ABSTRACT

In present work, we prepared Magnetite nanoparticles by coprecipitation of Fe^{2+} and Fe^{3+} with NH_4OH, further these magnetite core particles were coated with silica using tetra ethyl ortho silicate (TEOS). Then surface of silica coated magnetite nanoparticles was functionalized with aminopropyl groups using 3-aminopropyl trimethoxy silane (APTS) as a silylating agent. The morphology of the silica coated magnetite particles was observed to be spherical from SEM images. The hydrodynamic size was found to be 232 nm by dynamic light scattering. The cubic spinel structure for the magnetite nanoparticles were identified by X-ray diffraction studies. FTIR analysis shows that $–NH_2$ groups have been incorporated onto the surface of the magnetite nanoparticles by Fe-O-Si chemical bonds.

1. INTRODUCTION:

In last decades magnetic nanoparticle has become key components in different areas like bio separation in life science [1] biomedicine and bioengineering such as magnetically assisted drug delivery [2], cell isolation [3], MRI contrast agents [4], immunoassay [5] and bio macromolecule purification [6] due to their unique properties such as smaller size, high surface area, surface inertness, high oxidation potential, superparamagnetism, etc. The combination of magnetic switching behavior, with magnetic manipulation, separation and transportation to a desired location through the control of a magnetic field produced by an electromagnet or permanent magnet have created unique opportunities for enhancing the performance of magnetic nanoparticles such as 1) provide selective attachment to a functional molecule 2) can easily be separated from the medium by a simple magnetic process [7].

Although biomedical applications of magnetic nanoparticles have been reported extensively [8][9][10][11], but limited research on environmental applications were reported [12][13][14][15][16]. Heavy metals like Hg (II), Pb (II), Cd (II), and Cu (II), etc have toxic effect on human health and also have adverse effects on environment. Water pollution due to toxic heavy metals is almost found everywhere i.e. globally [17]. To reduce the discharge of heavy metals and to get clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal. Various processes like ion exchange, precipitation, membrane process, reverse osmosis, sedimentation; electrodialysis, adsorption, etc. are used for removal of heavy metal ions from water [18]. Amongst all these processes adsorption is the most preferable one for heavy metal ion removal.

Of the various magnetic materials reported in the literature for removal of heavy metal ions, iron oxides, mainly Fe_3O_4 have been the most widely used because of their simple preparation and Superparamagnetic nature. For removal of Cr (VI) magnetite [19] and maghemite [20] nanoparticles were applied to remove Cu(II) ions . At very low magnetic field gradients using magnetic separation method chitosan-bound Fe_3O_4 magnetic nanoparticles were prepared [21]. To remove arsenic from water monodisperse Fe_3O_4 nanocrystals were used [22]. By reducing the diameter of Fe_3O_4 nanocrystals to very smaller unit As (III) and As (V) could be removed efficiently. Self-assembled 3D flowerlike iron oxide nanostructure materials were found to have an excellent ability for the removal of As(V), Cr(VI), and Orange (II) from water[23]. More recently, superparamagnetic Fe_3O_4 nanoparticles with a surface functionalization of

dimercaptosuccinic acid were developed for the removal of toxic soft metals such as Hg, Ag, Pb, Cd, and Tl [24]. Recently for more efficient removal of heavy metal ions Fe_3O_4 coated with humic acid have been synthesized [25].

This Fe_3O_4 magnetite is generally of core shell type. Magnetic core is coated with inorganic shell i.e. silica. As first, silica formed on the surface of magnetic nanoparticles screens the magnetic dipolar attraction between magnetic nanoparticles, which favours the dispersion of magnetic nanoparticles in liquid media and protects them from leaching in an acidic environment. Second, due to the existence of abundant silanol groups on the silica layer, silica-coated magnetic nanoparticles can easily be activated with various functional groups [26]. The shells after functionalization with active groups can easily be complexed with heavy metals easily. Therefore, the investigation of magnetic nanoparticles with inorganic coating is of significance for applications. In this work we prepared magnetite nanoparticles coated with a near monolayer of amino silane, which has active group of - NH2 that can connect heavy metals easily. And the morphology, structure and composition of the coated magnetite nanoparticles were characterized by XRD, FTIR, SEM and Dynamic light scattering.

2. EXPERIMENTAL

2.1 Chemicals

The chemicals used for the synthesis of amino functionalized silica coated Fe_3O_4 magnetic nanoparticle were:

- Anhydrous $FeCl_3$ and $FeSO_4$,
- Trisodium citrate and NH_4OH,
- Tetra ethyl ortho silicate (TEOS),
- 3-Aminopropyl trimethoxy silane (APTS).

2.2. Synthesis of Fe_3O_4 magnetic Nanoparticles :

0.648g of $FeCl_3$ and 0.548g of $FeSO_4.6H_2O$ were taken.to which 40-45 ml of Millipore water was added under N_2 environment.5-10 ml of 25% NH_3 was added to the reaction mixture with continuous stirring and under nitrogen environment. And was kept for further stirring for1hr.100 ml of 0.3 molar trisodium citrate was added to the reaction mixture and again was allowed for stirring for another 30 min at 90 ^{0}C. The synthesized particles were collected using magnetic separator and was washed with (3×20 ml) Millipore water. Fe_3O_4 were again dispersed in Millipore water. [27]

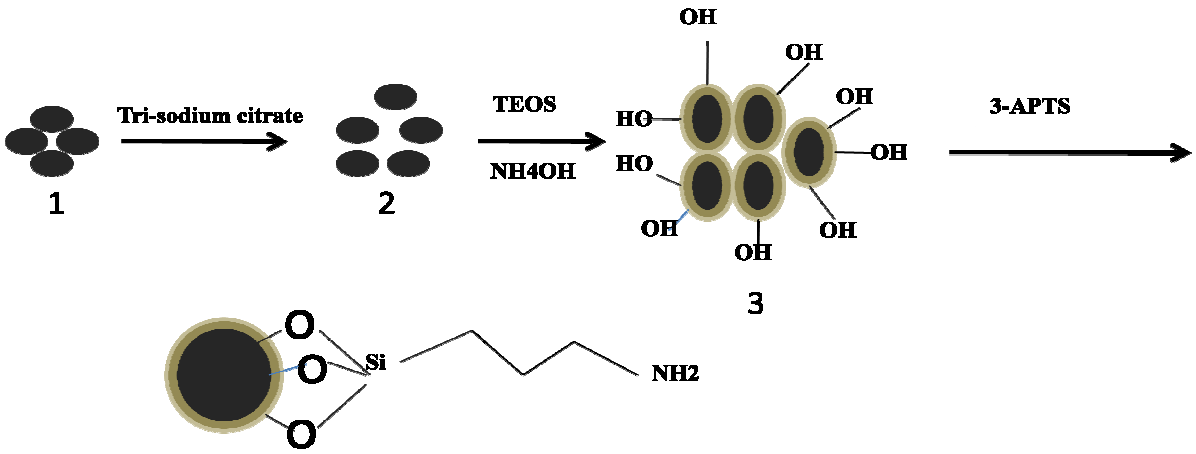
2.3. Synthesis of silica coated Fe_3O_4 magnetic Nanoparticles :

4g of the Fe_3O_4 despersed in Millipore water was taken in a solution of CH_3OH (160 ml) and 40 ml H_2O. To this reaction mixture 3ml of NH_3 solution and 2ml of tetraethyl orthosilicate(TEOS) were added one after another and was kept for stirring for further 24hr followed by washing with (2×30)ml Millipore water. Then dried at 80 ^{0}C and further heated at 400 ^{0}C. [27]

2.4. Synthesis of amino functionalized silica coated Fe_3O_4 magnetic Nanoparticles :

The silica coated magnetite nanoparticle was again dispersed in 25 ml ethanol and was diluted to 150 ml by ethanol and 1ml H_2O. The solution was then subjected to ultrasonic for 30min. Under rapid mechanical stirring 3-5 drops of 3-amino propyl trimethoxy silane

(APTS)was added to the solution and was kept for further stirring for 7h followed by washing with ethanol for five times. The product so formed was dried at 80^0C. [28]



Scheme 1: a schematic presentation of the whole reaction sequences involved in the synthesis of amino functionalized silica coated Fe_3O_4 magnetic nanoparticle. [27]

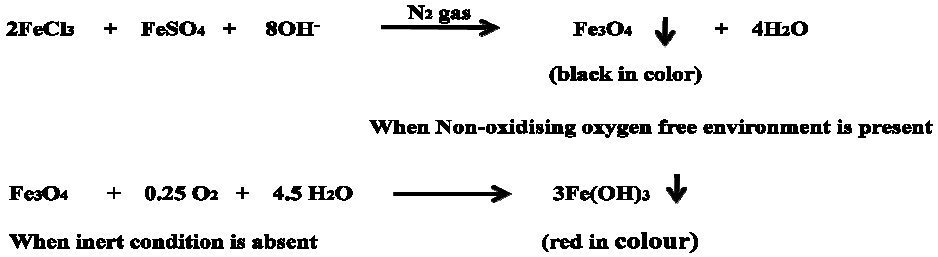
- The product 1 refers to the magnetite core shell i.e black ppt. of Fe_3O_4 magnetic nanoparticle synthesized by coprecipitation from Fe^{2+} and Fe^{3+} with NH_4OH as base.
- Product 2: Product1 was further stabilized by trisodiumcitrate which leads to a stable aqueous dispersion of Fe_3O_4 MNP.
- Product 3: Further Fe_3O_4 was silica coated using TEOS and ammonium hydroxide.
- Product 4: Then surface of product 3 was functionalized to active propyl groups by refluxing with 3-aminopropyl trimethoxy silane(APTS) in dry toluene. Here APTS act as silylating agent.

3. RESULTS AND DISCUSSION:

3.1. CHEMICAL REACTION INVOLVED:

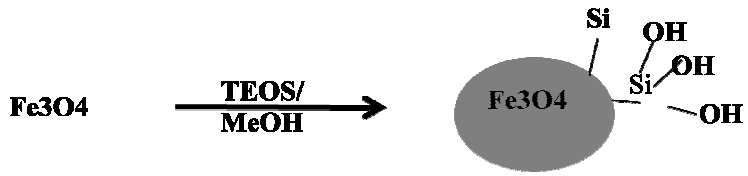
The scheme-1 represents the amino functionalization of silica coated magnetite nanoparticles involving following reaction steps

Product 1(Fe_3O_4 magnetic nanoparticle):

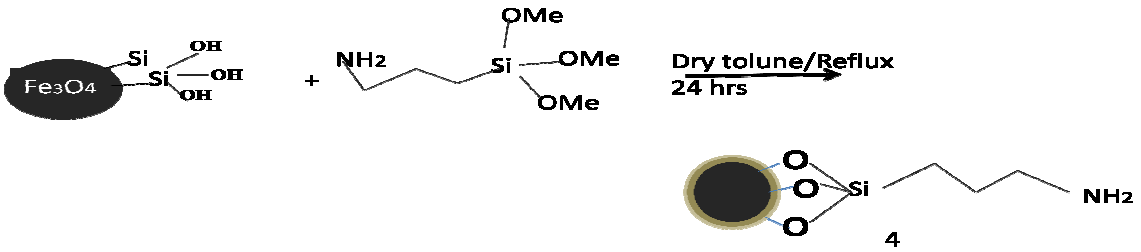


In absence of nitrogen environment the black precipitation of Fe_3O_4 undergoes oxidation to red precipitation of $Fe(OH)_3$. As a result the physical and chemical property of magnetic nanoparticles gets affected. So to prevent its further oxidation to unexpected product and agglomeration the reaction is carried out under inert environment between PH 4-9.

Product 3(silica coated Fe_3O_4 magnetic nanoparticle):



Product 4 (amino functionalized silica coated Fe_3O_4 magnetic nanoparticle):



3.2. CHARACTERIZATION:

The synthesized products were further characterized by SEM technique, XRD technique, DLS and FTIR analysis. The crystalline structure and spherical morphology of silica coated magnetite was identified from XRD and SEM respectively. To study the chemical bonds present in the products so formed were subjected to FTIR (Fourier Transform Infrared) analysis. Again further the particle size of magnetite core shell and silica coated magnetite was determined by Dynamic Light Scattering (DLS).

3.2.1. XRD

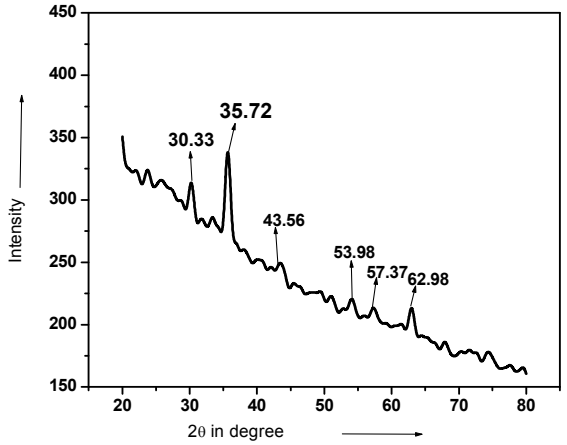


Figure 1(a): XRD pattern of Fe_3O_4 MNP

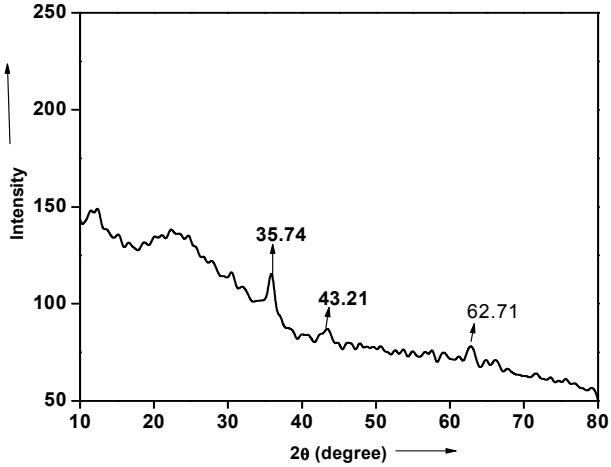


Figure 1(b): XRD pattern of Fe_3O_4@SiO2

Figure 1(a) illustrates the XRD patterns of black precipitations of Fe_3O_4 of magnetic nano particles. The position and relative intensity of all diffraction peaks match well with those of the magnetite (JCPDS 19-629) and broad peaks indicates nano-crystalline nature of the particles. Figure 1(b) shows XRD pattern of silica coated Fe_3O_4 magnetic nano-particle; the broad peak is due to amorphous silica. Peak at 10-20 degree coreesponds to SiO_2 and the rest of peaks are as those in XRD patterns of Fe_3O_4.

2Θ	D	[hkl]
30.3	2.96	[220]
35.7	2.53	[311]
43.5	2.09	[400]
53.7	1.71	[422]
57.5	1.61	[511]
62.9	1.48	[440]

3.2.2. SEM :

The spherical morphology of silica coated Fe_3O_4 magnetic nano-particle was identified by scanning electron microscopy as shown in figure2. From which the particle size was estimated to be approximately 200 nm.

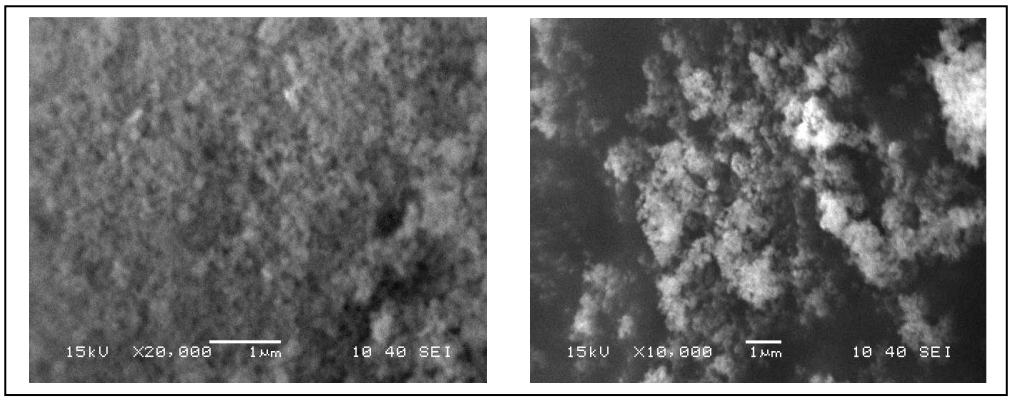


Figure 2: SEM images of silica coated Fe_3O_4 magnetic nanoparticle

3.2.3. DLS:

From DLS (Dynamic Light Scattering) the hydrodynamic size of the silica coated magnetite particle was found to be 232 nm from Figure 3(a) and that of magnetite core particle was found to be 148 nm from Figure 3(b).

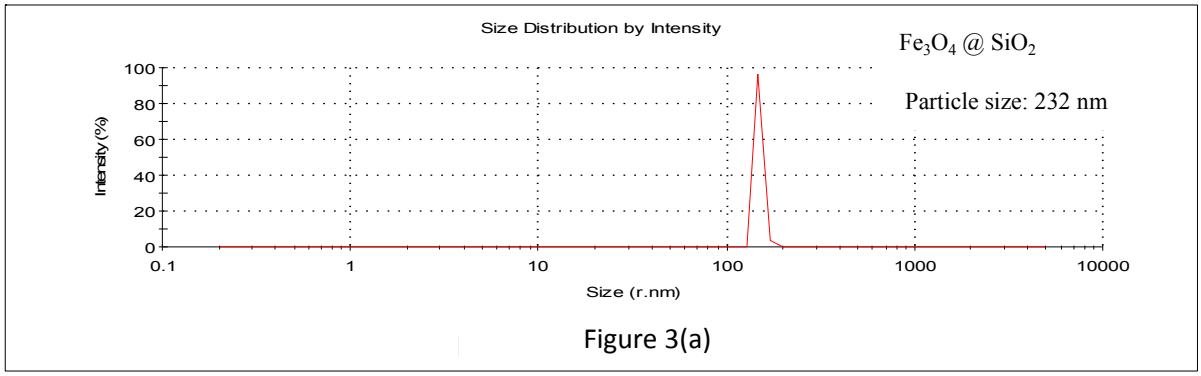


Figure 3(a)

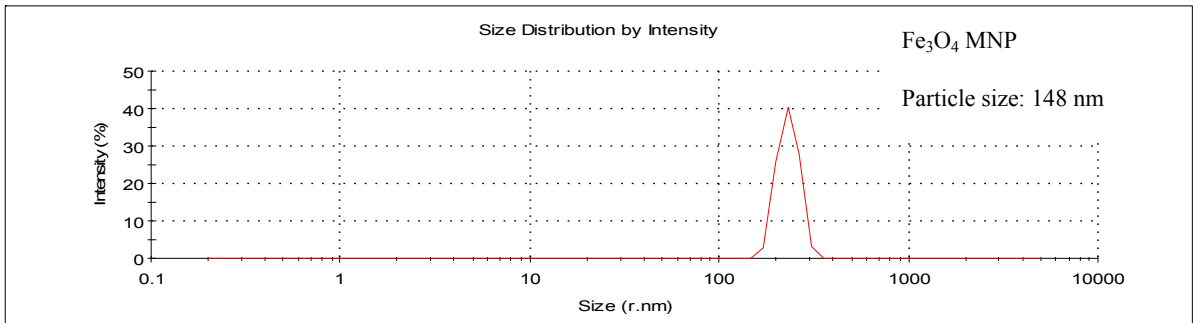


Figure 3(b)

3.2.4. FTIR:

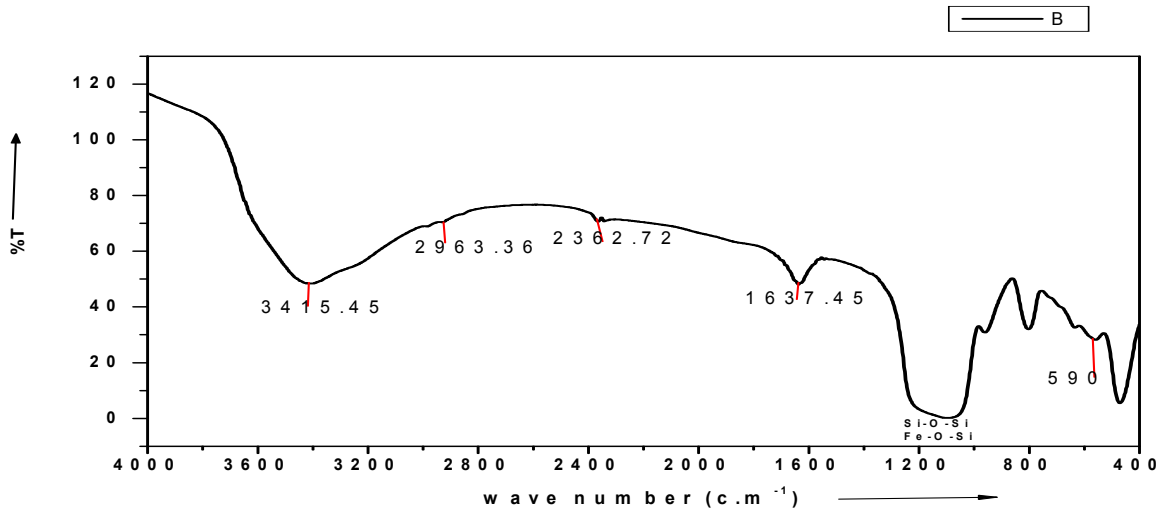


Figure 4(a)

Figure 4(a) illustrates the IR spectra of the silica coated magnetite, peaks at 590 cm^{-1} is for Fe-O stretching , 3650cm^{-1}- 3200cm^{-1} is for O-H bond stretching, the broad peak in range 1050 cm^{-1}-1250 cm^{-1} is for Si-O-Si and Fe-O-Si, peak at 2362 is for atmospheric CO_2.

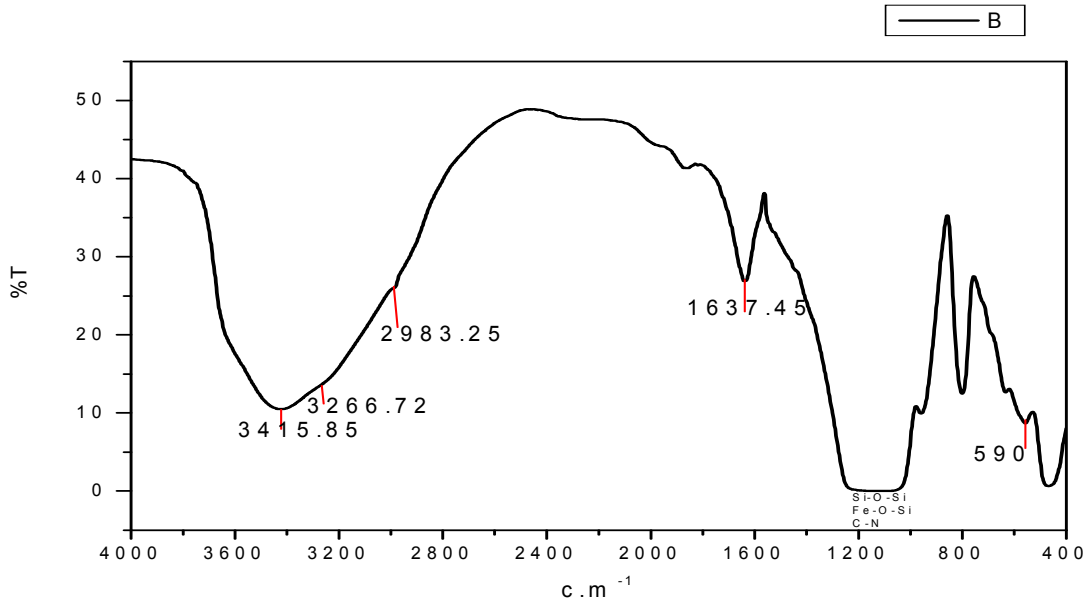


Figure 4(b)

Figure 4(b) illustrates the IR spectra of the 3-Aminopropyltrimethoxysilane coated on silica surface, peaks at 590 cm^{-1} is for Fe-O stretching , the broad peak in range 1050 cm^{-1}-1250 cm^{-1} is for Si-O-Si and Fe-O-Si, peak at 1637 cm^{-1} is for H-O-H bending vibration, peak at 2983 $cm^{-1}$is due to CH bond stretching of propyl groups and peak at 3500-3250 $c.m^{-1}$ is for NH bond stretching. This shows the surface functionalization to aminopropyl groups.

4. CONCLUSION:

Magnetite nanoparticles of hydrodynamic size 148 nm and silica coated magnetic nanoparticles of hydrodynamic size 232nm were synthesized successfully and characterized by XRD, SEM, DLS and FTIR analysis. Amine groups were introduced in the surface of magnetic silica nanoparticles by modifying with silylating agent 3-aminopropyltrimethoxy silane. FTIR spectra clearly indicate the formation of Fe-O-Si chemical bonds and the presence of amine propyl groups on the surface. Dynamic light scattering shows the presence of almost monodisperse particles both in case of magnetite and silica coated magnetic nanoparticles with excellent stability in aqueous medium. The separation of heavy metal ions such as Cu (II), Hg (II), Pb (II), etc. using amine functionalized silica coated magnetic nanoparticles is under investigation.

REFERENCES

1. A del Campo,T. sen, J.P Lellouche, I. J. Bruce, Multifunctional magnetite and silica-magnetite nanoparticles: Synthesis, surface activation and application in life sciences journal of magnetism and magnetic materials 293 (2005) 33-40
2. A.S. Lubbe, C.C. Alexiou, et al., J. Surg. Res. 95 (2001) 200.
3. A.L. Paul, G.R. Chandra, et al., J. Magn. Magn. Mater. 225 (2001) 301.
4. J. Halavaara, P. Tervahartiala, et al., Acad. Radiol. 43 (2002) 180.
5. M. Mary, U. Hafeli, W. Schutt, M. Zborowski (Eds.), Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, NewYork, 1997
6. A. Elaissari, M. Rodrigue, et al., J. Magn. Magn. Mater. 225 (2001)127.
7. L. Haining, Q. Binju, Y. Xiushen, L. Quan, L. Kangtaek, W. Zhijian, Boron adsorptionby composite magnetic particles, Chem. Eng. J. 151 (2009) 235–240
8. F. C. Meldrum, B. R. Heywood, S. Mann, Magnetoferritin: in vitro synthesis of a novel magnetic protein. Science 257(1992) 522–523
9. T. Tanaka, T. Matsunaga, Fully automated chemiluminescence immunoassay of insulin using antibody-protein a-bacterial magnetic particle complexes. Anal. Chem. 72 (2000) 3518–3522
10. J. W. M. Bulte, T. Douglas, B. Witwer, S.C. Zhang, E. Strable, B. K. Lewis, H. Zywicke, B.Miller, P. van Gelderen, B.M. Moskowitz, I. D. Duncan, J. A. Frank, Magnetodendrimers allow endosomal magnetic labeling and in vivo tracking of stem cells. Nat. Biotechnol.19 (2001) 1141–1147
11. J. M. Nam, C. S. Thaxton, C. A. Mirkin, Nanoparticle-based bio-bar codes for the ultrasensitive detection of proteins. Science 301(2003) 1884–1886
12. J. Hu, M. C. Lo, G. H. Chen, Removal of Cr (VI) by magnetite nanoparticles. Water Sci. Technol. 50 (2004) 139–146
13. J. Hu, G. Chen, I. M. C. Lo, Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. Water Res. 39 (2005) 4528–4536
14. Y.C. Chang,D.H. Chen, Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu(II) ions. J. Colloid Interface Sci. 283 (2005) 446–451

15. A.F. Ngomsik, A. Bee, M. Draye, G. Cote, V. Cabuil, Magnetic nano-and microparticles for metal removal and environmental applications: A review. C. R. Chimie 8 (2005) 963–970
16. C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Falkner, S. Yean, L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson, V. L. Colvin, Low-field magnetic separation of monodisperse Fe3O4 nanocrystals. Science 314 (2006) 964–967
17. J. O. Nriagu, J. M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 1988, 333, 134–139
18. N. Ahalya, T.V. Ramachandra Biosorption of Heavy Metals Res.J.Chem.Environ 7 (2003) 4
19. J. Hu, M. C. Lo, G. H. Chen, Removal of Cr (VI) by magnetite nanoparticles. Water Sci. Technol. 50 (2004) 139–146
20. J. Hu, G. Chen, I. M. C. Lo, Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. Water Res. 39 (2005) 4528–4536
21. Y.C. Chang, D.H. Chen, Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu (II) ions. J. Colloid Interface Sci. 283 (2005) 446–451
22. C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Falkner, S. Yean, L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson, V. L. Colvin, Low-field magnetic separation of monodisperse Fe3O4 nanocrystals. Science 314 (2006) 964–967
23. L.S. Zhong, J.S. Hu, H.P. Liang, A.M. Cao, W.G. Sun, L.J. Wan, Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. Adv. Master. 18 (2006) 2426-2437
24. W. Yantasee, C. L. Warner, T. Sangvanich, R. S. Addleman, T. G. Carter, R. J. Wiacek, G.E. Fryxell, C. Timchalk, M.G.Warner, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles.environ.Sci.Technol.41 (2007) 5114-5119
25. J. fuliu, Z. Shanzhao, A. Binjiang Coating Fe3O4 Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water. Received April 2, 2008. Revised manuscript received June 30, 2008. Accepted July 2, 2008

26. Y.H Deng, C.C Wang, J.H Hu, W.L Yang, S.K. Fu. Colloids and Surfaces A: Physicochem. Eng. Aspects 262 (2005) 87–93
27. S. Mohapatra, D. Pal, S.K. Ghosh and P. Pramanik J. Nanoscience and Nanotechnology 7 (2007)1-7
28. M. Ma et al., Colloids and Surfaces A: Physicochem. Eng. Aspects 212 (2003) 219-226